Spatial distribution of trace elements and impact on groundwater in a basin of calcareous Mediterranean soils

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1. Abstract

Groundwater represents a very significant source of fresh water for irrigation and drinking purposes and therefore preserving the availability and quality of this resource is extremely important. Trace elements in soil are not only part of its mineral composition but they can also accumulate in the top soil by anthropic activities and constitute a long-term environmental hazard. These elements can either be taken up by plants and re-enter the food chain, or leach from the top soil and thus endanger groundwater quality. The latter is of especial concern in intensive agricultural areas with increasing use of agrochemicals that receive heavy rainfall within relatively short periods, as is the case for the Mediterranean climate. Soil properties will have a mayor effect on elements mobility, whoever this mobility may be affected by the amount of water reaching the soil surface. Soils within the studied area cover a wide range of textural classes representative of the Mediterranean climate, with high content of calcium carbonate, low organic matter, and high spatial variability in soil properties as well as metals concentration. Results show that average yearly input of Pb can exceeds 500 g m^{-2} at sites close to the urban areas, while Cu and Zn contribution are 10 and 5 times lower respectively.

2. Introduction

Water management in agriculture is aiming for better tools to estimate risk assessment due to stricter legislation on soil and groundwater contamination, together with increasing population and demand in food production (UN Population Division 1997, Fischer and Heilig 1997). Trace elements in soil are not only part of its mineral composition but they can also accumulate in the top soil by anthropic activities and move down into the soil profile constituting a long-term environmental hazard. To evaluate this risk, it is necessary to account for a number of factors such as contaminant mobility, intrinsic variability in rainfall and evapotranspiration, and soil water retention and transmission characteristics.

Environmental risk assessment requires analysis of the chemical form of elements, that is to say, examination of their distribution within the soil solid phases. As in situ measurements remain expensive, trace metal bioavailability is more often indirectly estimated by selective or sequential extractions (Pueyo et al. 2003; Néel et al. 2007). On the other hand, drainage at the bottom of the soil profile is directly linked with both the driving atmospheric forcing and the physicochemical properties of the soil. Extreme climatic conditions such as intensive rains and droughts should be especially taken into account and soil properties should be spatially measured over extend areas in order to get good estimates of the spatial distribution of trace elements and its potential threat on reaching groundwater.

3. Material and Methods

This study focuses on elements Cu, Pb and Zn in an intensive agricultural area over calcareous Mediterranean soils in southern Spain. The area comprises approximately 200 km^2 and it lay on the Genil river basin. Soil properties (Table 1) were determined in laboratory using standard protocols on 55 samples within the area. Each sample includes 16 subsamples from every 900 m^2 on a systematic spaced sampling procedure. Drainage water at the bottom of the profile for each sampling site was estimated by means of a bucket-infiltration model (Fernández-Gálvez et al. 2007) which computes on a daily basis the inputs and outputs of soil water through rainfall and evaporation generated by a stochastic model of the local climate. Specific soil water retention and transmission characteristics were used at each site. Depth to water table was taken from the regional hydrogeological atlas (IGME, 1990). Trace metal mobility was evaluated by NaAc 1M extraction which represented the water-souble+exchangeable+ carbonate bound fractions (Campos et al. 1998). Extracted solutions were analyzed using ICP-AES. Total Cu, Pb and Zn content in the soil were also analytically measured at each sampling site.

4. Results and Discussion

Table 1 shows a brief summary of the soil analytical characteristics as well as the extracted metal fraction using sodium acetate. Only characteristics related with water retention in the soil profile are presented.

Table 1 Soil properties and extracted metal fraction with sodium acetate.

	Sand %	Slit %	Clay %	W1/3 %	W15 %	ρ g/cm^3	Organic C %	$CaCo_3$ %	Cu mg/kg	Pb mg/kg	Zn mg/kg
Mean	28	47	24	28	10	1.44	1.63	35.4	3.55	24.3	6.5
median	27	48	21	28	10	1.44	1.69	31.6	3.7	20.0	5.7
minimum	5	25	5	18	4	1.37	0.83	21.4	0.39	11.3	2.0
maximum	67	60	49	35	19	1.57	2.43	61.9	6.67	71.9	25.3

To elucidate the trace metal leaching in calcareous soils, the water-soluble fraction together with the exchangeable and carbonate bound fractions were considered as the potentially mobile metal species. Extracted metal results about 10% of the total content for Cu and Zn indicating that these metals are stored mainly by the soil compartment. However, extracted Pb represents 37% of the total content, a significant higher amount in soil solution. It is important to note that the amount of Cu, Pb and Zn given in Table 1 are expressed in mg of element per weight unit of dry soil, and in order to account for their mobility it is necessary to consider these concentrations in the soil solution at a water content equivalent to field capacity (W1/3, gravimetric water content at 33.3 kPa).

Consequently, among the considered elements, Pb presents the highest potential risk to pollute groundwater. If Pb mobility is expected to be fixed, exportation to groundwater would be proportional to the amount of water reaching the bottom of the unsaturated zone. This approximation represents the worst case scenario as for most soils there will be some sort of absorption along the profile depending on texture, mineralogy and interactions with the soil phases; and this has not been currently taking into account in the model. Yearly average water reaching groundwater obtained from 50 year simulations were used to compute inputs of Pb at each site. Figure 1 represents the contour plot obtained over the studied area for the average yearly inputs of Pb. The trend surface was computed by a least-squares algorithm with a third order polynomial surface. Inputs vary form almost negligible to values over 500 $g \cdot m^{-2} \cdot year^{-1}$. Although there are sites with water table at just one meter below the surface (West side of the aquifer, South to Lachar in Figure 1), higher average values are found close to the city of Granada and the metropolitan area around it, where water table is deeper but Pb concentration in soil is higher due to industrial activities and proximity to main roads.

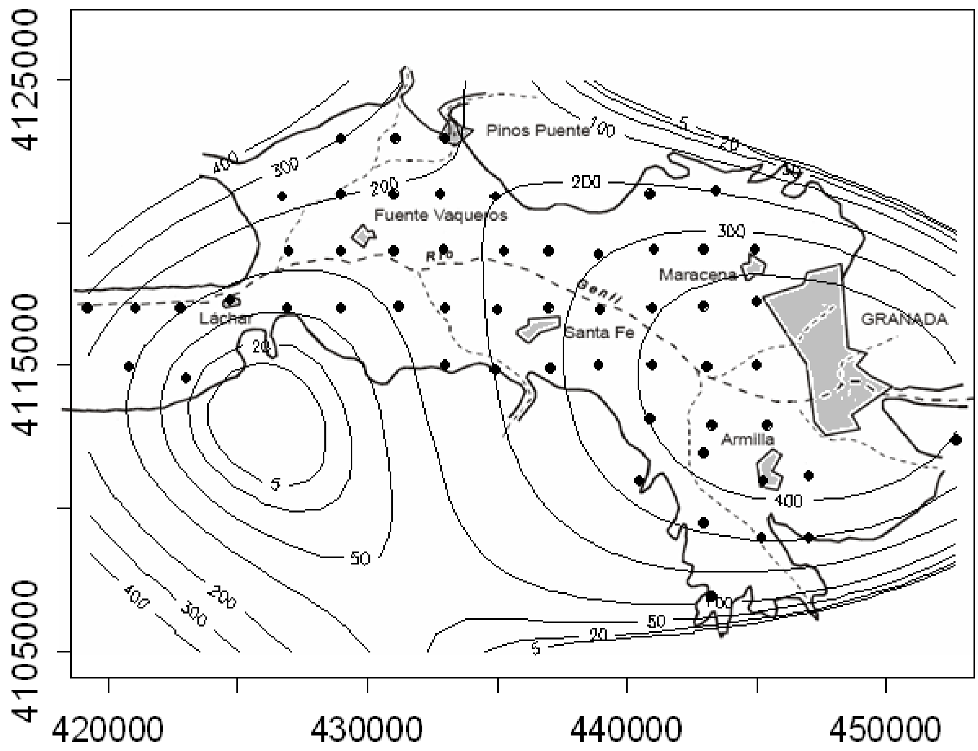

Figure 1 Average Pb ($g \cdot m^{-2} \cdot year^{-1}$) into groundwater. Axes are Easting and Northing in m. Black points represents soil sampling sites and urban areas are shown in grey.

Atmospheric driving forcing are fairly homogeneous over an are of 200 km^2 but soils in this case are very heterogeneous with a water holding capacity varying from 10 to 30%. Soil textures range from silty clay to sandy loam. At sites where soil water holding capacity is higher, water is normally kept closer to the soil surface and it is more easily accessible for evaporation, reducing the amount of water that drains deeper into the soil profile and therefore the potential threat to groundwater. The amount of coarse fragments (>2 mm) within the soil also has an affect on the movement of water, its low water retention capacity reduces evaporation and increases drainage, significantly modifying the soil water dynamics (Fernández-Gálvez et al. 2005).

5. Conclusions

Combined information from extracted metals in soil with NaAc 1M, a stochastic model of the local climate and in situ soil properties were used to assess the spatial distribution of Cu, Pb and Zn and its impact on groundwater in a basin of calcareous Mediterranean soils. Data reveal that Pb shows higher concentration around the area among the elements studied, especially close to the main urban areas. Leaching of these elements into the groundwater will increase concentration in the aquifer above WHO (2006) recommended levels for drinking water.

6. References

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